A STUDY OF THE VAPOR PRESSURES OF BINARY LIQUID MIXTURES IN RELATION TO VAN DER WAALS' EQUATION OF STATE

BY

IRVING ROBERT TANNENBAUM

B.S., Virginia Polytechnic Institute, 1946
M.S., Virginia Polytechnic Institute, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

Several equations of state proposed for non-ideal gases predict liquefaction. Because of its relative simplicity and also because of its relatively sound theoretical basis the equation of van der Waals[1] [equation (1)] has been widely used in predicting the properties of both gases and liquids.

$$(1) \qquad (p + n^2a/V^2)\ (V/n - b) = RT$$

In equation (1), p represents the pressure, V the volume, T the absolute temperature, n the number of moles, and R the universal gas constant. The constants a and b are introduced to take into account the intermolecular forces and the molecular volume, respectively.

It is the object of this paper to extend the work of Wall and Stent[2] in the consideration of binary liquid mixtures by taking into account the effects of the molecular volumes as well as the intermolecular forces.

Theoretical

On a purely thermodynamic basis the partial vapor pressures of binary mixtures of liquids obeying the van der Waals equation may be given by equations (2) and (3).

$$(2) \qquad \begin{aligned} ln\, p_1 = {} & ln(a/b^2) - a/bRT + lnX_1 \\ & + X_2[\,(da/adX_1 - 2db/bdX_1) \\ & - 1/RT\ (da/bdX_1 - adb/b^2dX_1)\,] \end{aligned}$$

$$(3) \qquad \begin{aligned} ln\, p_2 = {} & ln(a/b^2) - a/bRT + lnX_2 \\ & + X_1[\,(da/adX_2 - 2db/bdX_2) \\ & - 1/RT\ (da/bdX_2 - adb/b^2dX_2)\,] \end{aligned}$$

where X_i is the mole fraction of component i. In deriving

these equations the van der Waals constants a and b are defined as given in equations (4) and (5)

$$a = X_1^2 a_1 + 2X_1X_2a_{12} + X_2^2 a_2 \tag{4}$$

$$b = X_1^2 b_1 + 2X_1X_2b_{12} + X_2^2 b_2 \tag{5}$$

where a_1, a_2 and b_1, b_2 are the van der Waals constants for the pure components and where a_{12}, b_{12} are interaction constants characteristic of the mixture.

Equation (4) follows from a consideration of the possible modes of interaction of the molecules in a binary liquid mixture. Equation (5) is justified on a statistical basis.

For pure substances the van der Waals constant b is, theoretically, exactly four times the molar volume. In the case of mixtures this parameter becomes, similarly, four times the volume per "mole" of the mixture.

For any particular mixture the interaction constants a_{12} and b_{12} may be determined by simultaneous solution of equation (2) and equation (3) after substitution of experimental values for the vapor pressures at some given concentration.

A system of calculation is developed using Newton's method of approximation.[3] The empirical data needed are the vapor pressures of the pure components as a function of the temperature and the partial pressures of the mixture at some given composition.

Several sample calculations are presented graphically. The theory is found to agree quite well with observation. In most cases the agreement was within three percent and only rarely was the deviation greater than five percent. Greater accuracy, in most cases, was not obtained partially because of inconsistencies in the experimental data.

The theory is not applicable, however, to water or to other highly associated liquids. Association leads to erroneous results for the constants a and b partially because of a lack of knowledge of the precise definition of the term "mole" in such

a liquid and partially because the form of the van der Waals equation is not correct for liquids of this type. This effect is further complicated in binary liquid mixtures because the degree of association changes as the formal concentration is varied.

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VITA

Irving Robert Tannenbaum was born at Spring Lake, New Jersey on February 24, 1926 and received his elementary and secondary education in the public schools of Bradley Beach and Asbury Park, New Jersey and of Tucson, Arizona. After being graduated from the Asbury Park High School in 1943 he enrolled at the Virginia Polytechnic Institute. Upon receiving the degree of Bachelor of Science in Chemistry in 1946, he entered the Graduate Division of Virginia Polytechnic Institute. He completed the requirements for the degree of Master of Science in Chemistry in 1947 at which time he entered the Graduate College of the University of Illinois.

He was an instructor in Mathematics for one year at Virginia Polytechnic Institute and a teaching assistant in Physical Chemistry at the University of Illinois for two and one-half years. He was the Socony-Vacuum Oil Fellow in Chemistry for the academic year 1949-1950.

The author is a member of the American Chemical Society, Sigma Xi, and Phi Lambda Upsilon.

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